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(54) **Graft polyvinylidene fluoride copolymers**

(57) A graft copolymer suitable for adhering to a metal surface, consisting of a main polymer chain of polyvinylidene fluoride having 2 to 25% by weight of the copolymer of

grafts of acrylic acid or methacrylic acid polymer attached thereto.

This copolymer is obtained by graft polymerisation on to a polyvinylidene fluoride substrate pre-irradiated at at least 3×10^5 rads.

The copolymer is particularly recommended for the protection of metals used out of doors.

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SPECIFICATION**Graft polyvinylidene fluoride copolymers**

This invention relates to polyvinylidene fluoride copolymers, more particularly to copolymers of polyvinylidene fluoride (PVDF) treated so that, without any other intermediary, they will adhere directly to metal surfaces. The invention also relates to a method of producing such copolymers.

PVDF is known for its resistance to chemical agents, ultraviolet rays and abrasion. All these qualities make it an ideal material for use externally and particularly for protecting metals. This latter use, however, has not been entirely satisfactory, owing to the lack of direct adhesion of PVDF to metals. The only known PVDF-based coatings for metals always require the application of an intermediate bonding layer between the metal and the PVDF.

It has been found that the product obtained by grafting grafts of acrylic acid or methacrylic acid polymers on to a PVDF main chain not only retains the qualities of PVDF but also has the property of adhering directly to metals without any intermediate adhesive. A graft polymer of this kind is obtained by graft polymerisation of acrylic or methacrylic acid on to the macromolecular chain of PVDF. These polyacrylic chains are usually grafted on to a PVDF homopolymer. However, the homopolymer may be replaced by a copolymer containing at least 90% of vinylidene fluoride residues, these copolymers still retaining the properties of the PVDF homopolymer.

Graft polymerisation is known *per se*. It consists of contacting PVDF having active sites on its main chain with the graft initiating acrylic monomer for 4 to 12 hours at a temperature of from 50 to 80°C. The reaction is usually carried out in the presence of water containing a water-soluble inhibitor such as, for example, CuSO₄ or FeSO₄, in order to prevent, as far as possible, the formation of acrylic homopolymer which increases the viscosity of the graft polymerisation medium and which has to be separated off and discarded. The graft polymerisation may also be carried out in the presence of a PVDF solvent. In order to obtain a graft polymer having good adhesion to metals and retaining the properties of PVDF, it is recommended to graft to the main PVDF chain at least 2% by weight, of the total weight of graft polymer, of polyacrylic grafts. If grafting conditions are used which result in high levels of grafted methacrylic acid, it is possible to mix this graft product with untreated polymer to obtain solutions which yield adhesive coatings. The high grafting levels, particularly those exceeding 25% by weight of polyacrylic grafts on the main PVDF chain which are obtained with highly irradiated products, are not of much value, since PVDF is greatly degraded by excessive exposure to gamma radiation.

One of the ways of creating active sites on the main polymer chain is to irradiate the PVDF prior to the graft polymerisation. The irradiation of polyvinylidene fluoride is known and is described,

in particular, in U.S. Patent No. 4 137 137. Polyvinylidene fluoride is subjected, in air, to ionising radiation. In practice, this ionising radiation comes from a source of gamma or beta radiation. The dose required to ensure that effective grafting can be carried out is a minimum irradiation of the polyvinylidene fluoride at at least 3×10^5 rads. The polyvinylidene fluoride may be irradiated in the form of the crude polymer or already converted to a greater or lesser extent. Usually, to obtain maximum accessibility of the active sites, the polyvinylidene fluoride is irradiated in the form of a powder, the particle size of which may vary from 0.2 to 100 μ , or else in the form of filaments of at least 200 μ . After irradiation, the polyvinylidene fluoride can immediately be brought into contact with the monomer for the purpose of graft polymerisation, or else stored at a temperature usually below 10°C until the grafting is carried out.

The protection of the metals using the graft polymer is effected in the conventional manner customary in coating metal parts with thermoplastics. The coatings may be obtained by hot drying (a suitable temperature being 200°C) of a solution of graft PVDF in a solvent such as, for example, dimethylformamide, or a plastisol of the same graft PVDF in latent solvents such as dimethyl phthalate, diisobutyl ketone, isophorone, cyclohexanone or mixtures thereof. The coatings may also be obtained by projecting graft PVDF powder on to the metal surface, which has previously been heated to about 280—380°C; a number of applications of graft polymer, alternating with periods in the drying chamber, may be made so as to regulate the thickness of the coating. The coatings obtained adhere particularly well to steel, galvanised steel and aluminium. On this latter metal, the coatings will withstand 70 hours' immersion in water at 120°C without any apparent degradation.

Before the application of the coating, the metal sheets are preferably subjected to the surface treatments suitable for each metal which are generally carried out before the application of any coating or paint, such treatments include degreasing, sanding and combined treatments with phosphoric and chromic compounds.

The following Examples illustrate the present invention.

115 EXAMPLE 1

50 g of polyvinylidene fluoride in powder form obtained from a latex and irradiated at 0.8 Mrad, 93 g of water containing 7 g of methacrylic acid and 0.030 g of dissolved CuSO₄.5H₂O are placed in a stirred 500 cm³ container, in a nitrogen atmosphere. The mixture is heated to 60°C for 6 hours. The resultant grafted PVDF copolymer is separated by filtration, centrifuged, and washed with water on a filter, and then the product is dried in a drying chamber at 100°C.

54 g of dry polymer are recovered, containing 9.8% of methacrylic acid. The acid content is determined by alkali-metry with a solution of

methanolic potash, the graft polymer is dissolved in dimethylformamide, and 25% of water are added to the solution before titration. The end of neutralisation is monitored by means of the pH meter.

EXAMPLE 2

50 g of powdered polyvinylidene fluoride obtained from a latex irradiated at 0.5 Mrad, 100 g of water containing 5 g of methacrylic acid and 0.03 g of dissolved $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ are placed in the same reactor as in Example 1. The mixture is heated to 85°C for 6 hours.

15 The graft solid is separated by filtration, centrifuged, and washed by redispersing the product in water and filtering it again. It is then dried in the drying chamber at 120°C.

20 53.2 g of graft PVDF copolymer are recovered, containing 7.45% of methacrylic acid. The quantity of residual methacrylic acid is determined from the washing waters by acidimetry; 0.74 g of acid are found. By titration of the double bond, 0.72 g of methacrylic acid are found.

EXAMPLE 3

25 Each of the two graft polymers obtained in Examples 1 and 2 and the non-irradiated initial polyvinylidene fluoride are put into a 20% by weight solution in dimethylformamide. A fourth solution is also prepared by mixing, in equal amounts by weight, a portion of the solutions of 30 non-irradiated starting polymer and the polymer of Example 2. Small iron and aluminium plates which have been degreased, scoured with a phosphochromic mixture, rinsed and dried, are covered with these four solutions by steeping, 35 then dried in the oven for $\frac{1}{4}$ hour at 210°C. All the coatings adhere, with the exception of the one containing only the polyvinylidene fluoride, which can be removed from its substrate merely by scratching with a fingernail.

40 The other six plates are placed in an autoclave half-filled with water, and heated to 120°C for 72 hours. After this treatment, it is impossible even to begin to detach the coating, even by scraping it with a knife blade.

EXAMPLE 4

45 500 g of polyvinylidene fluoride obtained by suspension polymerisation, in the form of a powder of 40 to 100 μ with an apparent density of about 0.7, are placed in a stirred 2 litre reactor 50 under a nitrogen atmosphere. This polyvinylidene fluoride has been irradiated at 1 Mrad. 930 g of water containing 0.3 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 70 g of distilled methacrylic acid are also added. The mixture is heated to 60°C for 6 hours.

55 The graft solid is separated by filtration, centrifuged and washed with water on a filter, then dried in an oven at 120°C. A graft PVDF copolymer is recovered, having a methacrylic acid content of 12%.

60 Iron plates, degreased and scoured as before, are heated in an oven to 300°C, coated by sprinkling with the powdered non-irradiated initial

65 polyvinylidene fluoride and with powdered graft copolymer containing 12% of methacrylic acid. A number of cycles of sprinkling and placing in the oven are carried out until a coating with a thickness of about 200 μ is obtained. Finally, the plate is placed in the oven for 15 minutes and, as it is taken out of the oven, it is soaked in cold water. When scratched with a knife and thus broken open, the coating of the non-irradiated initial PVDF pulls away fairly easily, whereas the coating of graft polymer adheres perfectly, even after a period of 72 hours in water at 100°C.

EXAMPLE 5

70 100 g of PVDF obtained from a latex and irradiated at 1 Mrad, 200 g of water containing 10 g of acrylic acid and 0.05 g of dissolved $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ are placed in the reactor used for Example 1. The mixture is heated to 83°C for 6 hours.

75 The graft polymer is separated by filtration, centrifuged and washed with water on a filter, and then the product is dried in the oven at 100°C.

80 85 101.5 g of dry graft PVDF copolymer are recovered, containing 4.9% of acrylic acid, according to the acidity determination.

85 As indicated in Example 3, a 20% solution in dimethylformamide is prepared with the graft polymer, and this is used to coat an aluminium plate and a steel plate, which are baked in the oven at 210°C for 15 minutes. This coating of polymer grafted with acrylic acid is found to have the same good resistance to boiling water as the methacrylic acid grafts used in Example 3.

EXAMPLE 6

90 50 g of powdered polyvinylidene fluoride obtained from a latex and irradiated to 3 Mrads, 75 g of water containing 25 g of methacrylic acid and 0.025 g of dissolved $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ are placed in a stirred 500 cm^3 container in a nitrogen atmosphere. The mixture is heated to 60°C for 6 hours. The graft solid is separated by centrifuging, redispersed in water and centrifuged again, then 95 the product is dried in the oven at 100°C.

100 105 62 g of dry graft PVDF copolymer are recovered, containing 24% of methacrylic acid.

105 110 115 1 g of this product is placed with 5 g of pure, non-irradiated PVDF in solution in 30 g of dimethylformamide. Degreased aluminium plates are covered with the solution by soaking, then dried for $\frac{1}{4}$ hour at 210°C. The same qualities in boiling water are observed as for the other coatings of graft polyvinylidene fluoride used in Examples 3 and 5.

CLAIMS

120 1. A graft copolymer suitable for adhering to a metal surface, consisting of a main polymer chain of polyvinylidene fluoride having grafts of acrylic acid or methacrylic acid polymer, the polyacrylic grafts grafted to the main polyvinylidene fluoride chain amounting to from 2 to 25% by weight of the copolymer.

2. A graft copolymer according to Claim 1, substantially as described in any one of the foregoing Examples 1, 2 and 4 to 6.

3. A method of producing a graft polyvinylidene fluoride copolymer, the method comprising graft polymerising an acrylic monomer on to polyvinylidene fluoride which has been irradiated at at least 3×10^5 rads, the grafting being performed so that the weight of the resultant polymer side chains is from 2 to 25% by weight of the copolymer.

4. A method according to Claim 3, substantially as described in any one of the foregoing Examples 1, 2 and 4 to 6.

5. A metal substrate whenever coated with a

coating comprising a graft copolymer as claimed in Claim 1 or 2.

6. A metal substrate according to Claim 5, wherein the metal is steel, galvanised steel or aluminium.

7. A metal substrate according to Claim 5 or 6, wherein the coating has been formed from a solution of the graft copolymer in a solvent.

8. A metal substrate according to Claim 5 or 6, wherein the coating has been formed by projecting the graft copolymer onto the surface of the heated metal substrate.

9. A coated metal substrate according to Claim 5 substantially as described in any one of the foregoing Examples 3 to 6.